

Appendix 5

Supplementary Material for Chapter 5

Part B

Appendix M to 40CFR, Part 50

7. Appendix M is added to read as follows:

Appendix M to Part 50—Reference Method for the Determination of Particulate Matter as PM₁₀ in the Atmosphere

1.0 Applicability.

1.1 This method provides for the measurement of the mass concentration of particulate matter with an aerodynamic diameter less than or equal to a nominal 10 micrometers (PM₁₀) in ambient air over a 24-hour period for purposes of determining attainment and maintenance of the primary and secondary national ambient air quality standards for particulate matter specified in § 50.6 of this chapter. The measurement process is nondestructive, and the PM₁₀ sample can be subjected to subsequent physical or chemical analyses. Quality assurance procedures and guidance are provided in part 58, Appendices A and B of this chapter and in references 1 and 2 of section 12.0 of this appendix.

2.0 Principle.

2.1 An air sampler draws ambient air at a constant flow rate into a specially shaped inlet where the suspended particulate matter is inertially separated into one or more size fractions within the PM₁₀ size range. Each size fraction in the PM₁₀ size range is then collected on a separate filter over the specified sampling period. The particle size discrimination characteristics (sampling effectiveness and 50 percent cutpoint) of the sampler inlet are prescribed as performance specifications in part 53 of this chapter.

2.2 Each filter is weighed (after moisture equilibration) before and after use to determine the net weight (mass) gain due to collected PM₁₀. The total volume of air sampled, measured at the actual ambient temperature and pressure, is determined from the measured flow rate and the sampling time. The mass concentration of PM₁₀ in the ambient air is computed as the total mass of collected particles in the PM₁₀ size range divided by the volume of air sampled, and is expressed in micrograms per actual cubic meter (µg/m³).

2.3 A method based on this principle will be considered a reference method only if the associated sampler meets the requirements specified in this appendix and the requirements in part 53 of this chapter, and the method has been designated as a reference method in accordance with part 53 of this chapter.

3.0 Range.

3.1 The lower limit of the mass concentration range is determined by the repeatability of filter tare weights, assuming the nominal air sample volume for the sampler. For samplers having an automatic filter-changing mechanism, there may be no upper limit. For samplers that do not have an automatic filter-changing mechanism, the upper limit is determined by the filter mass loading beyond which the sampler no longer maintains the operating flow rate within specified limits due to increased pressure drop across the loaded filter. This upper limit cannot be specified precisely because it is a complex function of the ambient particle size distribution and type, humidity, filter type, and perhaps other factors. Nevertheless, all samplers should be capable of measuring 24-hour PM₁₀ mass concentrations of at least 300 µg/m³ while maintaining the operating flow rate within the specified limits.

4.0 Precision.

4.1 The precision of PM₁₀ samplers must be 5 µg/m³ for PM₁₀ concentrations below 80 µg/m³ and 7 percent for PM₁₀ concentrations above 80 µg/m³, as required by part 53 of this chapter, which

prescribes a test procedure that determines the variation in the PM₁₀ concentration measurements of identical samplers under typical sampling conditions. Continual assessment of precision via collocated samplers is required by part 58 of this chapter for PM₁₀ samplers used in certain monitoring networks.

5.0 Accuracy.

5.1 Because the size of the particles making up ambient particulate matter varies over a wide range and the concentration of particles varies with particle size, it is difficult to define the absolute accuracy of PM₁₀ samplers. Part 53 of this chapter provides a specification for the sampling effectiveness of PM₁₀ samplers. This specification requires that the expected mass concentration calculated for a candidate PM₁₀ sampler, when sampling a specified particle size distribution, be within ±10 percent of that calculated for an ideal sampler whose sampling effectiveness is explicitly specified. Also, the particle size for 50 percent sampling effectiveness is required to be 10±0.5 micrometers. Other specifications related to accuracy apply to flow measurement and calibration, filter media, analytical (weighing) procedures, and artifact. The flow rate accuracy of PM₁₀ samplers used in certain monitoring networks is required by part 58 of this chapter to be assessed periodically via flow rate audits.

6.0 Potential Sources of Error.

6.1 *Volatile Particles.* Volatile particles collected on filters are often lost during shipment and/or storage of the filters prior to the post-sampling weighing³. Although shipment or storage of loaded filters is sometimes unavoidable, filters should be reweighed as soon as practical to minimize these losses.

6.2 *Artifacts.* Positive errors in PM₁₀ concentration measurements may result from retention of gaseous species on filters^{4,5}. Such errors include the retention of sulfur dioxide and nitric acid. Retention of sulfur dioxide on filters, followed by oxidation to sulfate, is referred to as artifact sulfate formation, a phenomenon which increases with increasing filter alkalinity⁶. Little or no artifact sulfate formation should occur using filters that meet the alkalinity specification in section 7.2.4 of this appendix. Artifact nitrate formation, resulting primarily from retention of nitric acid, occurs to varying degrees on many filter types, including glass fiber, cellulose ester, and many quartz fiber filters^{5,7,8,9,10}. Loss of true atmospheric particulate nitrate during or following sampling may also occur due to dissociation or chemical reaction. This phenomenon has been observed on Teflon® filters⁸ and inferred for quartz fiber filters^{11,12}. The magnitude of nitrate artifact errors in PM₁₀ mass concentration measurements will vary with location and ambient temperature; however, for most sampling locations, these errors are expected to be small.

6.3 *Humidity.* The effects of ambient humidity on the sample are unavoidable. The filter equilibration procedure in section 9.0 of this appendix is designed to minimize the effects of moisture on the filter medium.

6.4 *Filter Handling.* Careful handling of filters between presampling and postsampling weighings is necessary to avoid errors due to damaged filters or loss of collected particles from the filters. Use of a filter cartridge or cassette may reduce the magnitude of these errors. Filters must also meet the integrity specification in section 7.2.3 of this appendix.

6.5 *Flow Rate Variation.* Variations in the sampler's operating flow rate may alter the particle

size discrimination characteristics of the sampler inlet. The magnitude of this error will depend on the sensitivity of the inlet to variations in flow rate and on the particle distribution in the atmosphere during the sampling period. The use of a flow control device, under section 7.1.3 of this appendix, is required to minimize this error.

6.6 *Air Volume Determination.* Errors in the air volume determination may result from errors in the flow rate and/or sampling time measurements. The flow control device serves to minimize errors in the flow rate determination, and an elapsed time meter, under section 7.1.5 of this appendix, is required to minimize the error in the sampling time measurement.

7.0 Apparatus.

7.1 PM₁₀ Sampler.

7.1.1 The sampler shall be designed to:

(a) Draw the air sample into the sampler inlet and through the particle collection filter at a uniform face velocity.

(b) Hold and seal the filter in a horizontal position so that sample air is drawn downward through the filter.

(c) Allow the filter to be installed and removed conveniently.

(d) Protect the filter and sampler from precipitation and prevent insects and other debris from being sampled.

(e) Minimize air leaks that would cause error in the measurement of the air volume passing through the filter.

(f) Discharge exhaust air at a sufficient distance from the sampler inlet to minimize the sampling of exhaust air.

(g) Minimize the collection of dust from the supporting surface.

7.1.2 The sampler shall have a sample air inlet system that, when operated within a specified flow rate range, provides particle size discrimination characteristics meeting all of the applicable performance specifications prescribed in part 53 of this chapter. The sampler inlet shall show no significant wind direction dependence. The latter requirement can generally be satisfied by an inlet shape that is circularly symmetrical about a vertical axis.

7.1.3 The sampler shall have a flow control device capable of maintaining the sampler's operating flow rate within the flow rate limits specified for the sampler inlet over normal variations in line voltage and filter pressure drop.

7.1.4 The sampler shall provide a means to measure the total flow rate during the sampling period. A continuous flow recorder is recommended but not required. The flow measurement device shall be accurate to ±2 percent.

7.1.5 A timing/control device capable of starting and stopping the sampler shall be used to obtain a sample collection period of 24 ±1 hr (1,440 ±60 min). An elapsed time meter, accurate to within ±15 minutes, shall be used to measure sampling time. This meter is optional for samplers with continuous flow recorders if the sampling time measurement obtained by means of the recorder meets the ±15 minute accuracy specification.

7.1.6 The sampler shall have an associated operation or instruction manual as required by part 53 of this chapter which includes detailed instructions on the calibration, operation, and maintenance of the sampler.

7.2 Filters.

7.2.1 *Filter Medium.* No commercially available filter medium is ideal in all respects for all samplers. The user's goals in sampling

determine the relative importance of various filter characteristics, e.g., cost, ease of handling, physical and chemical characteristics, etc., and, consequently, determine the choice among acceptable filters. Furthermore, certain types of filters may not be suitable for use with some samplers, particularly under heavy loading conditions (high mass concentrations), because of high or rapid increase in the filter flow resistance that would exceed the capability of the sampler's flow control device. However, samplers equipped with automatic filter-changing mechanisms may allow use of these types of filters. The specifications given below are minimum requirements to ensure acceptability of the filter medium for measurement of PM₁₀ mass concentrations. Other filter evaluation criteria should be considered to meet individual sampling and analysis objectives.

7.2.2 Collection Efficiency. ≥99 percent, as measured by the DOP test (ASTM-2986) with 0.3 μm particles at the sampler's operating face velocity.

7.2.3 Integrity. ±5 μg/m³ (assuming sampler's nominal 24-hour air sample volume). Integrity is measured as the PM₁₀ concentration equivalent corresponding to the average difference between the initial and the final weights of a random sample of test filters that are weighed and handled under actual or simulated sampling conditions, but have no air sample passed through them, i.e., filter blanks. As a minimum, the test procedure must include initial equilibration and weighing, installation on an inoperative sampler, removal from the sampler, and final equilibration and weighing.

7.2.4 Alkalinity. <25 microequivalents/gram of filter, as measured by the procedure given in reference 13 of section 12.0 of this appendix following at least two months storage in a clean environment (free from contamination by acidic gases) at room temperature and humidity.

7.3 Flow Rate Transfer Standard. The flow rate transfer standard must be suitable for the sampler's operating flow rate and must be calibrated against a primary flow or volume standard that is traceable to the National Institute of Standard and Technology (NIST). The flow rate transfer standard must be capable of measuring the sampler's operating flow rate with an accuracy of ±2 percent.

7.4 Filter Conditioning Environment.

7.4.1 Temperature range. 15 to 30 °C.

7.4.2 Temperature control. ±3 °C.

7.4.3 Humidity range. 20% to 45% RH.

7.4.4 Humidity control. ±5% RH.

7.5 Analytical Balance. The analytical balance must be suitable for weighing the type and size of filters required by the sampler. The range and sensitivity required will depend on the filter tare weights and mass loadings. Typically, an analytical balance with a sensitivity of 0.1 mg is required for high volume samplers (flow rates >0.5 m³/min). Lower volume samplers (flow rates <0.5 m³/min) will require a more sensitive balance.

8.0 Calibration.

8.1 General Requirements.

8.1.1 Calibration of the sampler's flow measurement device is required to establish traceability of subsequent flow measurements to a primary standard. A flow rate transfer standard calibrated against a primary flow or volume standard shall be used to calibrate or verify the accuracy of the sampler's flow measurement device.

8.1.2 Particle size discrimination by inertial separation requires that specific air velocities be

maintained in the sampler's air inlet system.

Therefore, the flow rate through the sampler's inlet must be maintained throughout the sampling period within the design flow rate range specified by the manufacturer. Design flow rates are specified as actual volumetric flow rates, measured at existing conditions of temperature and pressure (Q_a).

8.2 Flow Rate Calibration Procedure.

8.2.1 PM₁₀ samplers employ various types of flow control and flow measurement devices. The specific procedure used for flow rate calibration or verification will vary depending on the type of flow controller and flow rate indicator employed. Calibration is in terms of actual volumetric flow rates (Q_a) to meet the requirements of section 8.1 of this appendix. The general procedure given here serves to illustrate the steps involved in the calibration. Consult the sampler manufacturer's instruction manual and reference 2 of section 12.0 of this appendix for specific guidance on calibration. Reference 14 of section 12.0 of this appendix provides additional information on various other measures of flow rate and their interrelationships.

8.2.2 Calibrate the flow rate transfer standard against a primary flow or volume standard traceable to NIST. Establish a calibration relationship, e.g., an equation or family of curves, such that traceability to the primary standard is accurate to within 2 percent over the expected range of ambient conditions, i.e., temperatures and pressures, under which the transfer standard will be used. Recalibrate the transfer standard periodically.

8.2.3 Following the sampler manufacturer's instruction manual, remove the sampler inlet and connect the flow rate transfer standard to the sampler such that the transfer standard accurately measures the sampler's flow rate. Make sure there are no leaks between the transfer standard and the sampler.

8.2.4 Choose a minimum of three flow rates (actual m³/min), spaced over the acceptable flow rate range specified for the inlet, under section 7.1.2 of the appendix, that can be obtained by suitable adjustment of the sampler flow rate. In accordance with the sampler manufacturer's instruction manual, obtain or verify the calibration relationship between the flow rate (actual m³/min) as indicated by the transfer standard and the sampler's flow indicator response. Record the ambient temperature and barometric pressure. Temperature and pressure corrections to subsequent flow indicator readings may be required for certain types of flow measurement devices. When such corrections are necessary, correction on an individual or daily basis is preferable. However, seasonal average temperature and average barometric pressure for the sampling site may be incorporated into the sampler calibration to avoid daily corrections. Consult the sampler manufacturer's instruction manual and reference 2 in section 12.0 of this appendix for additional guidance.

8.2.5 Following calibration, verify that the sampler is operating at its design flow rate (actual m³/min) with a clean filter in place.

8.2.6 Replace the sampler inlet.

9.0 Procedure.

9.1 The sampler shall be operated in accordance with the specific guidance provided in the sampler manufacturer's instruction manual and in reference 2 in section 12.0 of this appendix. The general procedure given here assumes that the sampler's flow rate calibration is based on flow rates at ambient conditions (Q_a) and serves to illustrate the steps involved in the operation of a PM₁₀ sampler.

9.2 Inspect each filter for pinholes, particles, and other imperfections. Establish a filter information record and assign an identification number to each filter.

9.3 Equilibrate each filter in the conditioning environment (see 7.4) for at least 24 hours.

9.4 Following equilibration, weigh each filter and record the presampling weight with the filter identification number.

9.5 Install a preweighed filter in the sampler following the instructions provided in the sampler manufacturer's instruction manual.

9.6 (a) Turn on the sampler and allow it to establish run-temperature conditions. Record the flow indicator reading and, if needed, the ambient temperature and barometric pressure. Determine the sampler flow rate (actual m³/min) in accordance with the instructions provided in the sampler manufacturer's instruction manual.

(b) Note: No onsite temperature or pressure measurements are necessary if the sampler's flow indicator does not require temperature or pressure corrections or if seasonal average temperature and average barometric pressure for the sampling site are incorporated into the sampler calibration, under section 8.2.4 of this appendix. If individual or daily temperature and pressure corrections are required, ambient temperature and barometric pressure can be obtained by on-site measurements or from a nearby weather station. Barometric pressure readings obtained from airports must be station pressure, not corrected to sea level, and may need to be corrected for differences in elevation between the sampling site and the airport.

9.7 If the flow rate is outside the acceptable range specified by the manufacturer, check for leaks, and if necessary, adjust the flow rate to the specified setpoint. Stop the sampler.

9.8 Set the timer to start and stop the sampler at appropriate times. Set the elapsed time meter to zero or record the initial meter reading.

9.9 Record the sample information (site location or identification number, sample date, filter identification number, and sampler model and serial number).

9.10 Sample for 24±1 hours.

9.11 Determine and record the average flow rate (Q_a) in actual m³/min for the sampling period in accordance with the instructions provided in the sampler manufacturer's instruction manual. Record the elapsed time meter final reading and, if needed, the average ambient temperature and barometric pressure for the sampling period, in note following section 9.6 of this appendix.

9.12 Carefully remove the filter from the sampler, following the sampler manufacturer's instruction manual. Touch only the outer edges of the filter.

9.13 Place the filter in a protective holder or container, e.g., petri dish, glassine envelope, or manila folder.

9.14 Record any factors such as meteorological conditions, construction activity, fires or dust storms, etc., that might be pertinent to the measurement on the filter information record.

9.15 Transport the exposed sample filter to the filter conditioning environment as soon as possible for equilibration and subsequent weighing.

9.16 Equilibrate the exposed filter in the conditioning environment for at least 24 hours under the same temperature and humidity conditions used for presampling filter equilibration (see section 9.3 of this appendix).

9.17 Immediately after equilibration, reweigh the filter and record the postsampling weight with the filter identification number.

10.0 *Sampler Maintenance.*

10.1 The PM₁₀ sampler shall be maintained in strict accordance with the maintenance procedures specified in the sampler manufacturer's instruction manual.

11.0 *Calculations.*

11.1 Calculate the total volume of air sampled as:

$$V = Q_a t$$

where:

V = total air sampled, at ambient temperature and pressure, m³;

Q_a = average sample flow rate at ambient temperature and pressure, m³/min; and

t = sampling time, min.

11.2 (a) Calculate the PM₁₀ concentration as:

$$PM_{10} = (W_f - W_i) \times 10^6 / V$$

where:

PM₁₀ = mass concentration of PM₁₀, µg/m³;

W_f, W_i = final and initial weights of filter collecting PM₁₀ particles, g; and

10⁶ = conversion of g to µg.

(b) Note: If more than one size fraction in the PM₁₀ size range is collected by the sampler, the sum of the net weight gain by each collection filter [$\sum(W_f - W_i)$] is used to calculate the PM₁₀ mass concentration.

12.0 *References.*

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8. Appendix N is added to read as follows:

Appendix N to Part 50—Interpretation of the National Ambient Air Quality Standards for Particulate Matter

1.0 *General.*

(a) This appendix explains the data handling conventions and computations necessary for determining when the annual and 24-hour primary and secondary national ambient air quality standards for PM specified in § 50.7 of this chapter are met. Particulate matter is measured in the ambient air as PM₁₀ and PM_{2.5} (particles with an aerodynamic diameter less than or equal to a nominal 10 and 2.5 micrometers, respectively) by a reference method based on Appendix M of this part for PM₁₀ and on Appendix L of this part for PM_{2.5}, as applicable, and designated in accordance with part 53 of this chapter, or by an equivalent method designated in accordance with part 53 of this chapter. Data handling and computation procedures to be used in making comparisons between reported PM₁₀ and PM_{2.5} concentrations and the levels of the PM standards are specified in the following sections.

(b) Data resulting from uncontrollable or natural events, for example structural fires or high winds, may require special consideration. In some cases, it may be appropriate to exclude these data because they could result in inappropriate values to compare with the levels of the PM standards. In other cases, it may be more appropriate to retain the data for comparison with the level of the PM standards and then allow the EPA to formulate the appropriate regulatory response. Whether to exclude, retain, or make adjustments to the data affected by uncontrollable or natural events is subject to the approval of the appropriate Regional Administrator.

(c) The terms used in this appendix are defined as follows:

Average and *mean* refer to an arithmetic mean.

Daily value for PM refers to the 24-hour average concentration of PM calculated or measured from midnight to midnight (local time) for PM₁₀ or PM_{2.5}.

Designated monitors are those monitoring sites designated in a State PM Monitoring Network Description for spatial averaging in areas opting for spatial averaging in accordance with part 58 of this chapter.

98th percentile (used for PM_{2.5}) means the daily value out of a year of monitoring data below which 98 percent of all values in the group fall.

99th percentile (used for PM₁₀) means the daily value out of a year of monitoring data below which 99 percent of all values in the group fall.

Year refers to a calendar year.

(d) Sections 2.1 and 2.5 of this appendix contain data handling instructions for the option of using a spatially averaged network of monitors for the annual standard. If spatial averaging is not considered for an area, then the spatial average is equivalent to the annual average of a single site and is treated accordingly in subsequent calculations. For example, paragraph (a)(3) of section 2.1 of this appendix could be eliminated since the spatial average would be equivalent to the annual average.

2.0 *Comparisons with the PM_{2.5} Standards.*

2.1 *Annual PM_{2.5} Standard.*

(a) The annual PM_{2.5} standard is met when the 3-year average of the spatially averaged annual means is less than or equal to 15.0 µg/m³. The 3-year average of the spatially averaged annual means is determined by averaging quarterly means at each monitor to obtain the annual mean PM_{2.5} concentrations at each monitor, then averaging across all designated monitors, and finally averaging for 3 consecutive years. The steps can be summarized as follows:

(1) Average 24-hour measurements to obtain quarterly means at each monitor.

(2) Average quarterly means to obtain annual means at each monitor.

(3) Average across designated monitoring sites to obtain an annual spatial mean for an area (this can be one site in which case the spatial mean is equal to the annual mean).

(4) Average 3 years of annual spatial means to obtain a 3-year average of spatially averaged annual means.

(b) In the case of spatial averaging, 3 years of spatial averages are required to demonstrate that the standard has been met. Designated sites with less than 3 years of data shall be included in spatial averages for those years that data completeness requirements are met. For the annual PM_{2.5} standard, a year meets data completeness requirements when at least 75 percent of the scheduled sampling days for each quarter have valid data. However, years with high concentrations and more than a minimal amount of data (at least 11 samples in each quarter) shall not be ignored just because they are comprised of quarters with less than complete data. Thus, in computing annual spatially averaged means, years containing quarters with at least 11 samples but less than 75 percent data completeness shall be included in the computation if the resulting spatially averaged annual mean concentration (rounded according to the conventions of section 2.3 of this appendix) is greater than the level of the standard.

(c) Situations may arise in which there are compelling reasons to retain years containing quarters which do not meet the data completeness requirement of 75 percent or the minimum number of 11 samples. The use of less than complete data is subject to the approval of the appropriate Regional Administrator.

(d) The equations for calculating the 3-year average annual mean of the PM_{2.5} standard are given in section 2.5 of this appendix.

2.2 *24-Hour PM_{2.5} Standard.*

(a) The 24-hour PM_{2.5} standard is met when the 3-year average of the 98th percentile values at each monitoring site is less than or equal to 65 µg/m³. This comparison shall be based on 3 consecutive, complete years of air quality data. A year meets data completeness requirements when at least 75 percent of the scheduled sampling days for each quarter have valid data. However, years with high concentrations shall not be ignored just because they are comprised of quarters with less than complete data. Thus, in computing the 3-year